2004

Performance of Single Point Monitor in Measuring Ammonia and Hydrogen Sulfide Gases

Yi Liang
Iowa State University

Hongwei Xin
Iowa State University, hxin@iastate.edu

Steven J. Hoff
Iowa State University, hoffer@iastate.edu

Tom L. Richard
Pennsylvania State University

Brian J. Kerr
United States Department of Agriculture

PERFORMANCE OF SINGLE POINT MONITOR IN MEASURING AMMONIA AND HYDROGEN SULFIDE GASES

Y. Liang, H. Xin, S. J. Hoff, T. L. Richard, B. J. Kerr

ABSTRACT. *Performance of Single Point Monitors (SPMs) was evaluated for measuring aerial ammonia (NH_3, 0 to 30 ppm) and hydrogen sulfide (H_2S, 0 to 90 ppb) under laboratory and field conditions. Calibration gas or NH_3/H_2S−ladden air at various dew−point temperatures (t_{dp}) were introduced simultaneously to the SPMs under evaluation and a chemiluminescence NH_3 analyzer or a pulsed−fluorescence H_2S analyzer. Coefficient of variation for "as−is" readings among the SPMs, a measurement of unit interchangeability, was up to 15% for H_2S and up to 25% for NH_3. Linear relationships existed between readings of the SPMs and those of the respective gas analyzer, with the slope increasing with moisture content of the calibration or sample air. Specifically, H_2S readings by the SPMs averaged, respectively, 66%, 80%, 87%, and 97% of those by the analyzer for calibration gas at t_{dp} of −22°C (dry), 9°C, 13°C, and 16°C. In comparison, NH_3 readings by the SPMs averaged 42%, 86%, 102%, and 178% of those by the analyzer for calibration gas at t_{dp} of −22°C, 8.5°C to 10°C, 12.5°C to 14°C, and 16°C to 17°C, respectively. Correctional equations were developed to compensate for the moisture interference effect on SPM readings of both gases. The corrected SPM readings for H_2S measurement with an overall correctional equation generally achieved 90% to 107% agreement with the respective analyzer readings. However, such corrections for NH_3 measurements proved not as effective (59% to 90% agreement). To improve the quality of H_2S data obtained with SPMs moisture content of the sample air should be concurrently measured and moisture compensation can be made using an overall correctional equation.*

Keywords. *Animal feeding operation, Ammonia, Hydrogen sulfide, Gas sensors, Air quality monitoring, Moisture interference.*

Air pollutants, such as ammonia (NH_3), nitrous oxide (N_2O), methane (CH_4), hydrogen sulfide (H_2S), carbon dioxide (CO_2), and particulate matter (PM), are generally associated with animal feeding operations (AFOs). Ammonia and H_2S have received particular attention due to their heath effects on humans. As the need to determine gas concentrations and emission rates increases, various measurement methods and instruments have evolved. Colorimetric detection tubes have been used to measure NH_3 concentrations in swine, dairy and broiler facilities (Chung et al., 1996; Zhu et al., 2000; Stowell et al., 2002). Jerome® H_2S analyzers have been used to measure H_2S concentration in swine, dairy and broiler facilities (Zhu et al., 2000; Stowell et al., 2002) and in beef cattle feedlots (Rhoades et al., 2003; Koelsch et al., 2004). Chemiluminescence NH_3/nitric oxide (NO) analyzers have been used to measure NH_3 concentrations in both UK and US livestock buildings (Wathes et al., 1997; Demmers et al., 1999; Jacobson et al., 2003). Concentrations of NH_3, CH_4, and N_2O in exhaust air from manure storage have been measured with a photoacoustic multi−gas monitor (Hansen et al., 2003) and evaluated with colorimetric detector tubes. Fourier transform infrared analyzer (FTIR) has also been used to measure emissions of NH_3, N_2O and CH_4 from dairy housing (Amon et al., 2001). Hinz and Linke (1998) measured NH_3 concentrations from various livestock buildings with both a photoacoustic multi−gas monitor and an FTIR spectrometer as a comparison. The authors concluded that deviations in measured NH_3 levels (4− to 8−ppm range) between the two different devices were negligible ($R^2 = 0.9287$). To date, information has been relatively meager from systematic comparisons of different measurement techniques that are suitable for agricultural air quality applications.

Single Point Monitors (SPMs) (Model 7100, Zellweger Analytics, Inc., Lincolnshire, Ill.) have been used to monitor NH_3 and H_2S levels in or around swine facilities (Bicudo et al., 2002; Predicala et al., 2001; Schmidt et al., 2002). The SPM measures gas levels based on the rate of color change of a chemical cassette tape that reacts with the target gas. The color intensity change of the tape is sensed by a photocell whose output is then converted to analog output and digital display of the gas level. The advantages of SPM include its relatively low cost (~$7000), portability for field application, and ability to detect relatively low gas concentrations. The main drawbacks and concerns about validity of the data obtained with SPMs include their large uncertainty (20% to 25% per manufacturer's specification), susceptibility to

rticle was submitted for review in March 2004; approved for publication by the Biological Engineering Division of ASAE in September 2004.

Mention of company or product name is for presentation clarity and does not imply endorsement by the authors or their affiliated institutions or exclusion of other suitable products.

The authors are **Yi Liang, ASAE Member Engineer,** Post−Doctoral Research Associate, **Hongwei Xin, ASAE Member Engineer,** Professor, **Steven J. Hoff, ASAE Member Engineer,** Associate Professor, Agricultural and Biosystems Engineering Department, Iowa State University, Ames, Iowa; **Tom L. Richard, ASAE Member Engineer,** Associate Professor, Agricultural and Biological Engineering Department, Pennsylvania State University, State College, Pennsylvania; and **Brian J. Kerr,** Research Leader, USDA/ARS, Ames Iowa. **Corresponding author:** Hongwei Xin, 3204 National Swine Research and Information Center (NSRIC), Iowa State University, Ames, IA 50011−3310; phone: 515−294−4240; fax: 515−294−4250; e−mail: hxin@iastate.edu.

measurement interference by moisture content in the sample air, and the inability to calibrate the units in the field or by the user. The interchangeability of the SPM units also is largely unknown. Nonetheless, SPMs have been used by certain states (e.g. Minnesota) for checking compliance of state air quality standards. SPM is an approved method for measuring ambient H_2S by the Minnesota Pollution Control Agency.

The objective of this study was to evaluate and characterize operational performance of SPMs with regard to measurement uncertainty, repeatability, stability, interference with moisture, and interchangeability in measuring aerial NH_3 and H_2S under laboratory and field conditions. The potential effect of ambient temperature on H_2S readings was also checked.

Materials and Methods

Laboratory Evaluation System

A laboratory evaluation and verification system was set up to evaluate SPMs for the anticipated measurement ranges of NH_3 and H_2S (fig. 1). Inserting a "chem−key," which adjusts measurement time and internal calibration according to a factory−set algorithm, sets the range span for these SPMs. The chem−keys for NH_3 evaluation had a range of 0 to 30 ppm. In this range, SPMs update the display and analog output every 15 s. The range of chem−keys for H_2S evaluation was 0 to 90 ppb with an updating interval of 15 min. Amines and hydrides chemcassettes (part no. 700342 and 700300, respectively, Zellweger Analytics) were used to evaluate NH_3 and H_2S, respectively. Calibration gases at various known concentrations were simultaneously introduced to the SPMs and the respective gas analyzer.

A chemiluminescence NH_3/NO analyzer (Model 17C, Thermo Environmental Instruments, Franklin, Mass.) and a pulsed−fluorescence H_2S/SO_2 analyzer (Model 450TCL, TEI) were used as the comparison or reference analyzers, with their measurement ranges set at 0− to 30−ppm NH_3 and 0− to 100−ppb H_2S, respectively. Use of these gas analyzers as the comparison references was because they are commonly used as the "standard" measurement instruments by regulatory agencies, such as the U.S. EPA. The NH_3/NO analyzer uses an external vacuum pump to create a sample flow rate of 0.6 LPM. The H_2S/SO_2 analyzer uses an internal diaphragm pump to create a sample flow rate of 1.1 LPM. Zero and span calibrations or verifications of the analyzers were performed daily. Each SPM is equipped with an internal sampling pump. The flow rates of all SPM units were checked by connecting a rotameter upstream of SPM units and found to be 0.4∼0.5 LPM. Dew−point temperature (t_{dp}) of the sample air was measured with a chilled mirror dew point hygrometer (−50°C to 50°C, ±0.2°C, Model 2000, EG & G, Burlington, Mass.).

The calibration gas distribution system consisted of a Teflon® manifold, fittings, and tubing (Teflon FEP) (fig. 1). The column−shaped manifold measured 444 mm (17.5 in.) long, 40 mm (1.57 in.) outside diameter, and 10 mm (0.39 in.) inside diameter, with 24 ports on the side and 1 port at each end. The two end ports of the manifold were both connected by a T−connector to the calibration gas source to minimize

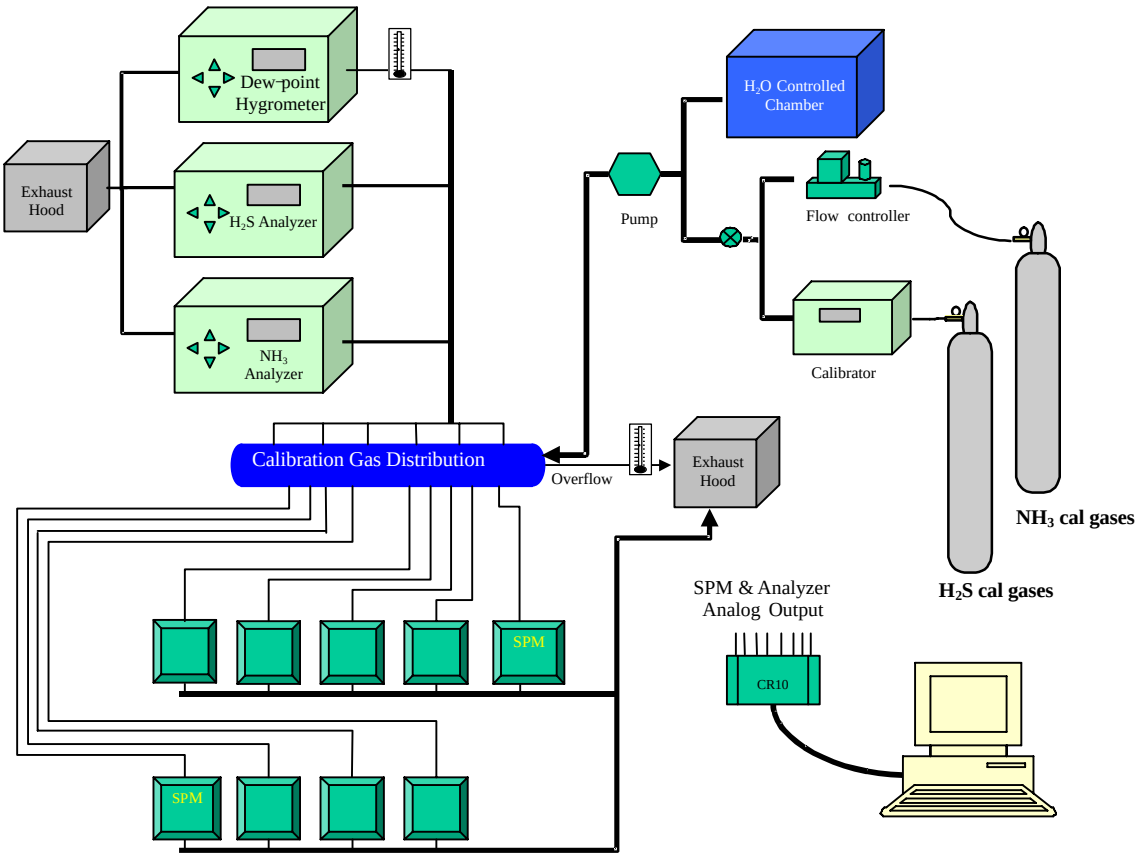

Figure 1. A schematic representation of the lab system setup for Single Point Monitor (SPM) evaluation.

possible variability due to port position. Nine of the 24 ports on the side were used as inlets for a group of nine SPMs tested simultaneously (a total of 44 SPMs were tested in five batches). Three more ports were connected to a Teflon filter that was shared by both analyzers, a dew point hygrometer, and an excess flow bypass. The number of ports used, and thus SPMs involved per test, were limited by the flow volume available from the diluting system that delivers the source gas. The remaining ports were plugged. Teflon tubing of 1.5∼1.8 m (5∼6 ft) in length was used to supply test gas from the manifold to each SPM unit as well as to the gas analyzers. Variability among the ports was checked by rotating a SPM through six ports that represented all possible distances from the ends of the manifold and there was none.

Analog outputs from the SPMs (4 to 20 mA) and the analyzers (0 to 1 VDC) were sampled at 2−s intervals and stored as either 1−min averages (H_2S tests) or 3−s averages (NH_3 tests) using a measurement and control module (Model CR10, Campbell Scientific, Inc., Logan, Utah). Channels of the measurement module were individually calibrated for both types of target gases.

Calibration gases of 4.8−ppm H_2S (+N_2 balance, ±2% accuracy) and 233−ppm NH_3 (+air balance, ±2% accuracy) (Matheson Tri−Gas Inc., La Porte, Tex.) were used to generate various gas concentrations used for the lab evaluation.

Lab Evaluation – Target Gases in Dry Air

Dry calibration air was generated with a dynamic span gas diluting calibrator (Model 700, Advanced Pollution Instrumentation, Inc., San Diego, Calif.) and a zero air generator (Model 701, API). The dynamic diluting calibrator was programmed to generate dry (t_{dp}= −22°C) H_2S calibration gas at nominal concentrations of 0, 10, 20, 40, 60, or 70 ppb. Selection of a concentration for testing was randomized in the evaluation process.

Because the dynamic diluting calibrator was unable to dilute 233−ppm NH_3 gas to the desired range of 0 to 30 ppm, a mass flow controller (0 to 1 LPM, stainless steel wetted parts, AALBORG Instruments & Controls, Inc, Orangeburg, N.Y.) was connected to the NH_3 calibration gas cylinder to control the desired NH_3 gas flow rate, while the dynamic diluting calibrator was used to generate dry zero air. The NH_3 gas and dry zero air were mixed to achieve the concentrations of 0, 5, 10, 15, 20, or 25 ppm. Selection of a concentration for testing was randomized in the evaluation process.

The SPMs were randomly divided into five groups. It took 15 min for the SPM to update the display when monitoring H_2S gas at concentrations up to 90 ppb. Four updates were collected for each H_2S level, with the first update discarded in data analysis. For the dry H_2S calibration air evaluation, each group of tests took 6 h, and the 44 units were tested in five days. According to the manufacturer, H_2S chemcassette tape expires in 30 days once the sealed package is opened and each tape can run continuously for more than 30 days. Nine tapes were used and rotated among all units for the dry gas test. When tests were not in session, the tapes were stored in a 4°C (39°F) cold room, per manufacturer's recommendation.

The SPMs updated readings every 15 s when monitoring NH_3 gas. Exposure of the SPMs to an equilibrated concentration continued for 3 min before changing to the next level. Each group of SPMs was tested for six concentrations, completed in 1 h, before switching to the next group. The NH_3 chemcassette tape expires in 30 days once the sealed package is opened and each tape can run continuously for approximately 16 h. Nine tapes were used and rotated among all units for the dry gas tests, which was completed in two days.

Lab Evaluation – Target Gases in Humid Air

A temperature− and humidity−controlled room at the National Swine Research and Information Center (LEAP Lab II, Ames, Iowa) was instrumented to carry out the lab evaluation of target gases in humid air. Three dew−point temperatures (t_{dp}) at a dry−bulb temperature of 24.4°C and four concentration levels (including zero), in a factorial arrangement, were chosen for testing each target gas. Dew−point temperature in the room was controlled at about 9°C, 13°C, or 16°C. Nominal concentrations of 0−, 12−, 35−, or 70−ppb H_2S and 0, 5−, 15−, or 25−ppm NH_3 were chosen for the tests.

The desired gas concentrations were achieved by proportionally mixing the dry calibration gas with the fresh air from the environmentally controlled room. Since t_{dp} of the humid fresh air remained reasonably constant, t_{dp} of the humid calibration air reaching the manifold fluctuated within 2°C for NH_3 and 0.5°C for H_2S. As with the dry gas evaluation, SPMs were tested in five groups, with the H_2S test finished in 10 days and the NH_3 test finished in 4 days.

Lab Evaluation – Temperature Effect

The SPMs have a factory−recommended operating temperature range of 0 to 40°C. To check the potential temperature effect on their performance, four SPMs were placed inside an incubator (Fisher Scientific, Inc., Hampton, N.H.) set at 10°C, 20°C, or 30°C ambient temperature. Dry H_2S calibration gas (t_{dp}= −22°C at nominal levels of 0, 10, or 70 ppb was used in the evaluation that was completed in two days.

Field Evaluation

Eight SPMs were randomly selected to monitor NH_3 gas at a poultry production site on 17 October 2003. Air samples from the exhaust stream were introduced into the distribution manifold and monitored simultaneously by the chemiluminescence analyzer and the SPMs. Six of the eight SPMs were set to update the output or readings at 15−s intervals, whereas the remaining two were set to be on a 15−min duty cycle, i.e., update the readings every 15 min. Two SPMs stopped working shortly after the onset of the test. The tapes of these two units and the tapes from the 15−min duty cycle units were removed after the test and stored in a 4°C cold room and were re−used for the subsequent test.

Six SPMs were then used to monitor NH_3 concentration near a swine facility on 14 and 17 November 2003 since concentrations encountered in the field poultry test were quite low (4 ppm). Due to a restriction in available flow rate, SPMs in groups of three were appended to an existing air quality monitoring system for the test. Air samples inside the building were introduced to the manifold and monitored simultaneously by the chemiluminescence analyzer and the SPMs.

Ten SPMs were randomly selected to monitor H_2S concentration near the swine facility between 19 November and 5 December 2003. Air sampled at 1−m downstream of an exhaust fan was introduced to the manifold and monitored by both the pulsed−fluorescence analyzer and the SPMs. Data of the SPMs and the pulsed−fluorescence analyzer were recorded at 5−min intervals using the same CR10 module as used in the lab tests.

Data Analysis

Two potential factors contribute to the discrepancy in measurement by the SPM and the analyzer, i.e., inherent resolution of the SPM and interference caused by moisture in sample air. Furthermore, the degree of moisture interference may depend on the gas level. Hence, to correct the SPM readings of moist air samples, the "as−is" readings were first converted to the equivalent dry readings; followed by correcting the dry readings of SPM to the corresponding analyzer readings. The following functional relationships were used to relate the SPM reading to the analyzer value:

$$C_{ref} = (C_{SPM\_dry} - \beta)/m \quad (1)$$

$$C_{SPM\_dry} = C_{SPM\_as-is} - \Delta C_{SPM} \quad (2)$$

$$\Delta C_{SPM} = a + b\times\Delta t_{dp} + c\times C_{SPM\_as-is} + d\times\Delta t_{dp}\times C_{SPM\_as-is} \quad (3)$$

$$C_{corrected} = (C_{SPM\_as-is} - \Delta C_{SPM} - \beta)/m \quad (4)$$

where

- C_{ref} = concentration indicated by the analyzer, considered as the "reference" value
- C_{SPM_dry} = concentration indicated by the SPM under dry air condition
- C_{SPM_as-is} = concentration indicated by the SPM under moist condition
- β, m = intercept and slope, respectively, of linear regression equation at dry air condition
- ΔC_{SPM} = change in concentration due to moisture interference of SPM
- a, b, c, d = regression coefficients
- Δt_{dp} = change in dew−point temperature between moist and dry sampling/calibration air/gas
- $C_{corrected}$ = corrected concentration based on "as−is" readings, Δt_{dp}, and regression coefficients

Statistical analysis was performed using the SAS GLM procedure to detect the effect of three ambient temperatures on SPM readings.

The field measurements from each SPM and the respective analyzer were paired for comparison. For H_2S, the pairs were formed at 15−min intervals. Three recordings from the pulsed−fluorescence analyzer during the 15−min sampling interval immediately prior to the corresponding SPM 15−min update was selected and averaged as the respective analyzer reading. For NH_3, 15−s data were averaged into 1−min data before analysis was performed. Hourly averages were also analyzed and tested for significant difference between each SPM and the respective analyzer using two−tailed paired t−test.

Stability Evaluation

To evaluate the stability of the SPMs, laboratory tests using H_2S calibration gas were conducted 8 months after the initial evaluation, during which a majority of the units were employed periodically in field monitoring with accumulated usage of 3 to 4 weeks. Twenty−five SPMs were randomly selected and evaluated with dry H_2S calibration gas (t_{dp}= −22˚C) at nominal levels of 0, 10, 20, 40, 60, or 70 ppb. For each unit, the change in SPM readings at the six nominal levels was calculated based on the two sets of data as shown in equation 5. A new set of linear regression equations were developed for the 25 SPMs. Statistical analysis was performed (SAS GLM procedure) to compare differences in slopes or intercepts between the two regression equations for each SPM.

$$\text{Change}(\%) = \frac{|\,H_2S_{new} - H_2S_{old}\,|}{H_2S_{old}}\times 100 \quad (5)$$

Results and Discussion

Lab Evaluation – Hydrogen Sulfide

A total of 44 SPMs were tested under dry air condition and 43 SPMs were tested under humid air condition (one malfunctioned during test) for H_2S. Means and standard deviations (S.D.) of H_2S readings by the SPMs and the pulsed−fluorescence analyzer are shown in table 1. The within−units S.D. column shows the variation among three consecutive updates of the SPMs, whereas the among−units S.D. column reflects the variability or interchangeability among the units. It was observed that the three consecutive updates by the same SPM for a given calibration gas level varied up to 6 ppb (up to 16% of the SPM reading) at relatively high concentrations (60 ppb) (table 1). This result indicates the rather poor repeatability of the SPMs. The among−units coefficient of variation (CV) ranged from 9.3% to 15.4% for concentrations of 10 to 70 ppb, but was much greater (up to 215%) at zero concentrations.

Table 1. Summary of Single Point Monitor (SPM) readings for various calibration H_2S concentrations and dew−point temperature in laboratory conditions.

Dew−Point Temperature (°C)	Analyzer Concentration (ppb)	H_2S Readings by SPM and Statistics				
		Mean	Within Units[a]		Among Units	
		(ppb)	S.D.	CV (%)	S.D.	CV (%)
−22	0	0.97	0.99	101	0.74	76.3
	9.52	8.52	0.50	5.84	1.03	12.1
	19.5	15.7	0.62	3.93	1.84	11.7
	39.3	30.8	0.81	2.62	3.21	10.4
	59.6	40.3	1.76	4.36	4.24	10.5
	69.9	47.2	1.47	3.11	4.38	9.27
9	0.04	1.07	0.17	15.9	1.34	125
	11.6	11.0	0.36	3.31	1.49	13.6
	35.9	29.5	0.91	3.08	4.22	14.3
	66.8	54.8	1.69	3.09	7.25	13.2
13	0.04	0	0	N/A	0	N/A
	11.5	11.6	0.37	3.22	1.35	11.7
	35.2	31.6	0.91	2.89	3.78	12.0
	65.3	57.3	1.59	2.77	6.76	11.8
16	0.04	0.12	0.21	177	0.26	214
	11.3	12.5	0.52	4.20	1.77	14.2
	34.8	35.2	1.11	3.15	5.42	15.4
	64.7	63.2	2	3.16	7.34	11.6

[a] S.D. = standard deviation; CV = coefficient of variation.

Comparisons in H_2S readings by the SPMs and the pulsed−fluorescence analyzer at the tested t_{dp} are shown in figure 2. Generally, SPM readings were lower for all the tested concentrations except for the dry zero air. However, the SPM readings increased with increasing moisture content. The regression equations relating SPM and analyzer H_2S concentrations at each t_{dp} level were of the following forms:

For t_{dp}=−22°C, $[H_2S, ppb]_{SPM}$ =

$$0.655[H_2S, ppb]_{Analyzer} + 2.36 \ (R^2 = 0.9931) \quad (6)$$

For t_{dp} = 9°C, $[H_2S, ppb]_{SPM}$ =

$$0.802[H_2S, ppb]_{Analyzer} + 1.11 \ (R^2 = 0.9996) \quad (7)$$

For t_{dp} = 13°C, $[H_2S, ppb]_{SPM}$ =

$$0.8739[H_2S, ppb]_{Analyzer} + 0.57 \ (R^2 = 0.9990) \quad (8)$$

For t_{dp} = 16°C, $[H_2S, ppb]_{SPM}$ =

$$0.9734[H_2S, ppb]_{Analyzer} + 0.72 \ (R^2 = 0.9991) \quad (9)$$

Hence, when using SPMs to measure the change in H_2S concentration under dry air condition (t_{dp} = −22°C), the result will be about 66% of that measured using the respective analyzer. Under moist air conditions with t_{dp} of 9°C, 13°C, and 16°C, the result will be about 80%, 87%, and 97%, respectively, of the analyzer values.

Lab Evaluation – Ammonia

A total of 45 units were evaluated for NH_3 measurement and the results are shown in table 2. The among−units CV ranged from 5% to 25% for concentrations of 0 to 26 ppm. Two units were excluded from the regression analysis due to spurious performance under test conditions with this gas.

Comparisons in NH_3 readings by the SPMs and the chemiluminescence analyzer at the tested t_{dp} are shown in figure 3. Generally, under dry air conditions the readings by the SPMs were slightly higher than those by the analyzer for concentrations of 0 and 5 ppm, but lower for other tested concentrations (11, 16, 21, or 26 ppm). The regression equations relating the NH_3 measurement by the SPMs and the analyzer at each t_{dp} level had the following forms:

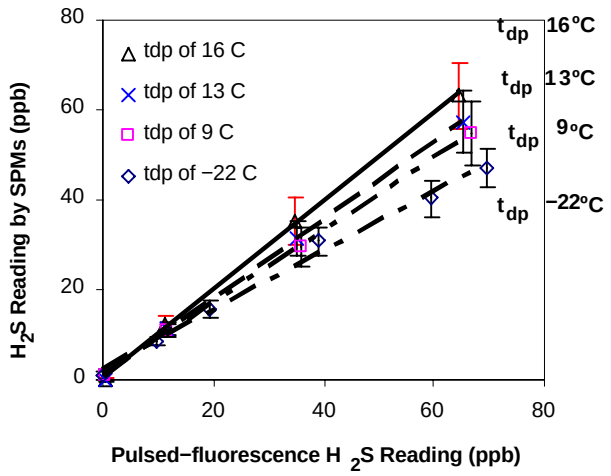

Figure 2. Comparison of H_2S measurements by SPMs (43 units) and the pulsed−fluorescence analyzer for the selected concentrations of calibration gas at dew−point temperature (t_{dp}) of −22°C, 9°C, 13°C, and 16°C. The vertical bars of the data points represent standard deviations.

Table 2. Summary of Single Point Monitor (SPM) readings for various calibration NH_3 concentrations and dew−point temperature in laboratory conditions.

Dew−Point Temperature (°C)	Reference Concentration (ppm)	NH_3 Readings by SPM and Statistics				
		Mean (ppm)	Within Units[a]		Among Units	
			S.D.	CV (%)	S.D.	CV (%)
−22	0.03	2.96	0.08	2.70	0.24	8.16
	5.24	5.73	0.13	2.19	0.48	8.41
	10.9	8.32	0.21	2.55	0.70	8.42
	16.5	11.1	0.46	4.11	0.92	8.34
	21.5	12.4	0.29	2.34	0.83	6.73
	25.8	13.8	0.40	2.88	0.72	5.25
8.5−10	0	0.02	0	0	0.06	396
	5.53	8.31	0.33	3.97	1.52	18.3
	13.8	15.8	1.22	7.71	1.47	9.31
	23.7	20.8	1.59	7.64	2.72	13.1
12.6−14	−0.02	0.01	0	6.84	0.07	958
	5.68	12.3	0.50	4.06	2.10	17.1
	13.8	21.7	1.00	4.61	2.86	13.2
	23.3	24.4	1.15	4.73	2.30	9.41
16−17	0.03	0.09	0.02	22.9	0.42	453
	5.49	14.7	0.66	4.51	2.47	16.8
	9.54	22.0	1.00	4.57	3.53	16.1
	13.6	23.8	1.08	4.53	5.91	24.9

[a] S.D. = standard deviation; CV = coefficient of variation.

For t_{dp} = −22°C, $[NH_3, ppm]_{SPM}$ =

$$0.4182[NH_3, ppm]_{Analyzer} + 3.46 \ (R^2 = 0.9866) \quad (10)$$

For $t_{dp} \approx$ 9°C, $[NH_3, ppm]_{SPM}$ =

$$0.8559[NH_3, ppm]_{Analyzer} + 2.01 \ (R^2 = 0.9494) \quad (11)$$

For $t_{dp} \approx$13°C, $[NH_3, ppm]_{SPM}$ =

$$1.0186[NH_3, ppm]_{Analyzer} + 3.72 \ (R^2 = 0.8749) \quad (12)$$

For $t_{dp} \approx$16°C, $[NH_3, ppm]_{SPM}$ =

$$1.7818[NH_3, ppm]_{Analyzer} + 2.37 \ (R^2 = 0.9222) \quad (13)$$

Hence when using SPM to measure the change in NH_3 concentration under t_{dp} of −22°C (dry air), 9°C, 13°C, and 16°C, the result will be, respectively, 42%, 86%, 102%, and 178% of the analyzer values.

The seemingly quadratic relationships between the SPM and the NH_3 analyzer readings under humid conditions, as shown in figures 4b−d, were at least partially attributed to the experimental procedure. Namely, for a given t_{dp} in the humidity−controlled room, sample air of higher NH_3 concentration required relatively larger proportion of the dry calibration gas, which resulted in somewhat lower humidity (lower t_{dp}) in the mixed sample air. This lower t_{dp} sample air presumably caused relatively lower SPM readings. In other words, the four points displayed in figure 3b−d were collected under progressively declining t_{dp} of sample air (10.2°C to 8.6°C in fig. 4b; 14.4°C to 12.6°C in fig. 3c; 17.6°C to 16.7°C in fig. 3d). The linear relationship between the SPM and the analyzer readings at dry conditions is shown in

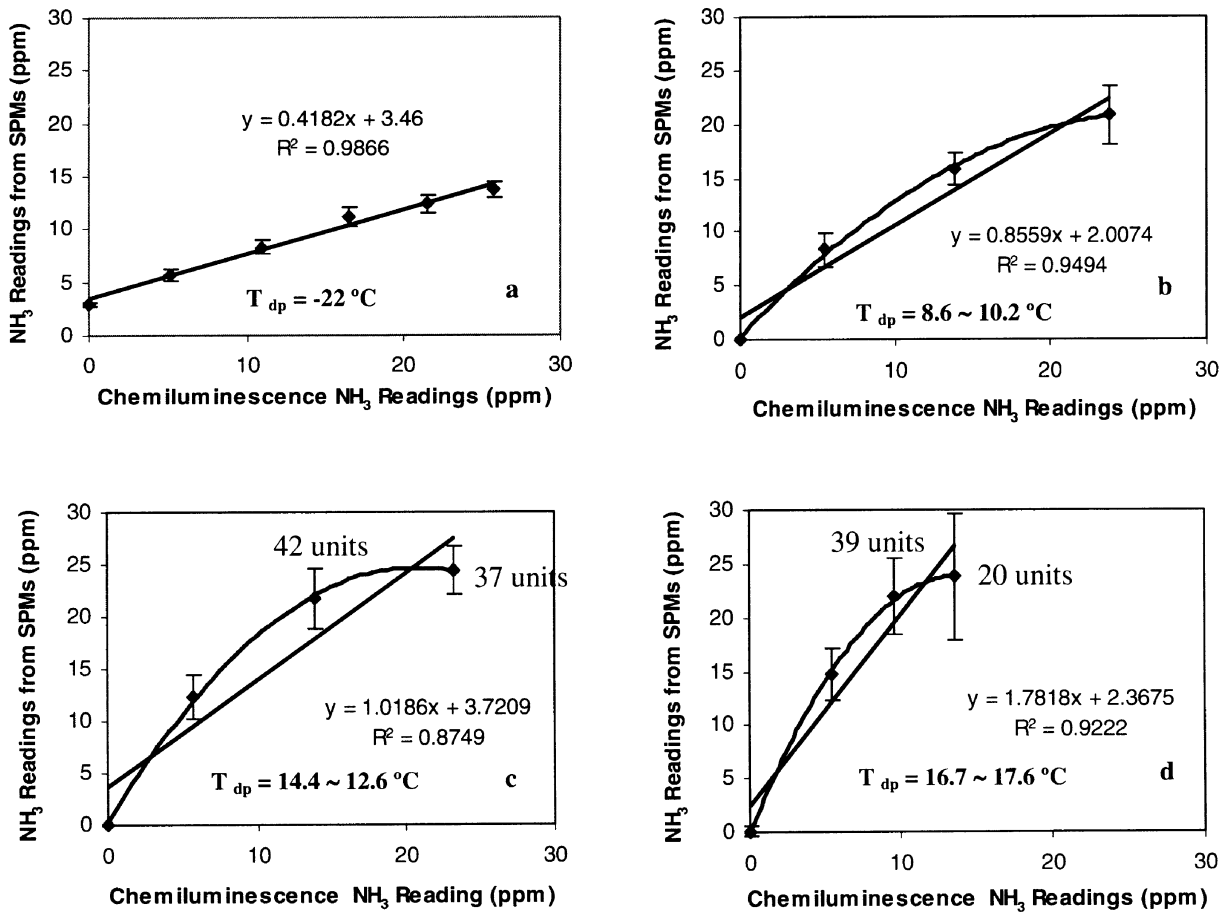

Figure 3. Comparison of NH_3 measurements by SPM units and chemiluminescenceanalyzer at selected concentrations of calibration gas and dew−point temperature (t_{dp}) of a) −22°C; b) 10.2°C, 9.9°C, 9.3°C, 8.6°C progressively; c) 14.4°C, 14.0°C, 13.5°C, 12.6°°C progressively; and d) 17.6°C, 17.3°C, 17.0°C, 16.7°C progressively. The vertical bars represent standard deviations. Values were averaged from 45 units unless otherwise labeled.

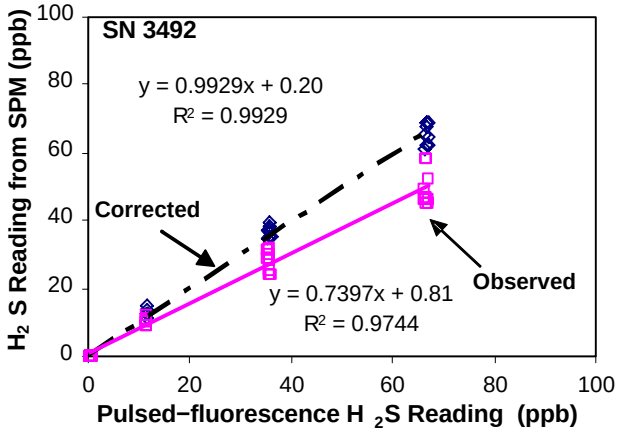

Figure 4. Comparison of H_2S concentrations (SN 3492) before and after correction for moisture content in the sample air.

figure 3a. The actual t_{dp} values were used in subsequent analysis of moisture interference on NH_3 readings by the SPMs (discussed later).

Less than 43 data points were involved in calculating the average readings for the last two points of figure 3c−d. Specifically, when t_{dp} was about 13°C (fig. 3c), 20% of the SPMs displayed the "30+" out of range error at an analyzer reading of 24 ppm NH_3. When t_{dp} was about 16°C (fig. 3d), the "30+" out of range error occurred to 90% of the SPMs at >14 ppm NH_3, thereby resulting in a shorter curve.

Temperature Effect

Hydrogen sulfide concentrations measured by four SPMs at ambient temperatures of 10°C, 20°C, or 30°C are presented in table 3. Significant differences were observed at 0 ppb ($P < 0.001$) but not at 10 or 70 ppb. However, it was unclear whether the significant differences at zero air resulted from temperature effect, inherent uncertainty of readings, or detection limit at the zero level.

Regression Analysis of Individual Units

For each type of gas, 43 regression equations (of eq. 3 form) were established to correct SPM readings to the analyzer reading levels. Examples of results before and after correction of the SPM readings under humid conditions

Table 3. Effect of ambient temperature on hydrogen sulfide measurement by Single Point Monitor (SPM) (mean and standard deviation of four replicates).

H_2S Concentration (ppb)	Ambient Temperature (°C)		
	10	20	30
0	0.1 ± 0.2[a]	1.5 ± 0.6[a]	2.4 ± 0.3[a]
10	7.8 ± 0.2	8.1 ± 0.3	7.9 ± 0.3
70	38.9 ± 1.2	38.0 ± 0.4	38.4 ± 2.8

[a] Significant at $P < 0.001$.

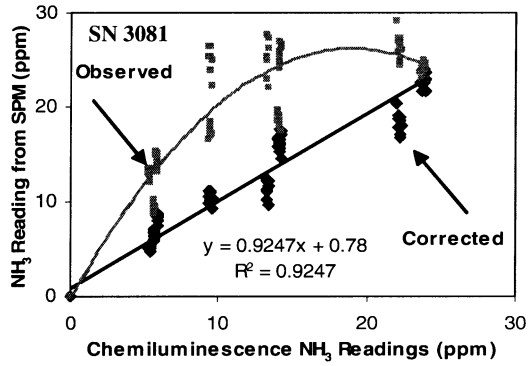

Figure 5. Comparison of NH_3 concentrations (SN 3081) before and after correction for moisture content in the sample air.

(t_{dp}= 8~16°C) were compared and are plotted in figure 4 (H_2S) and figure 5 (NH_3). The corrected H_2S concentrations (from eq. 4) generally showed a linear trend ($R^2 > 0.99$), having a slope close to 1 and an intercept less than 1 (fig. 4). In comparison, the corrected NH_3 concentrations had a larger variability, as evidenced by the lower R^2 value of 0.92 (vs. 0.99 for H_2S).

Interchangeability and Overall Regression for Hydrogen Sulfide

Interchangeability among the SPMs was examined for H_2S gas. Because the usefulness of individual regressions for NH_3 gas was marginal, unit interchangeability was not investigated for this gas. Since readings by all SPMs exhibited linear relationships with those of the respective analyzer, slopes obtained under the dry air testing conditions were chosen as a parameter to characterize each unit's behavior and unit interchangeability. The histogram in figure 6 shows the distribution of 44 slopes of the linear regression equations relating SPM H_2S readings to the pulsed−fluorescence analyzer values.

Among the 44 SPMs tested under dry air, 34 (77%) of them had a slope of 0.6∼0.7, averaging 0.65. Three units (7%) had a slope of 0.48, 0.79, or 0.84. The considerably wide range of slopes and relatively large among−units CV (tables 1 and 2) demonstrate the weak interchangeability among the SPMs.

Regression analysis was performed on the H_2S data collected from all SPMs in an attempt to derive a general correctional equation. A closer examination of the operational performance of the SPMs led to exclusion of three units from the overall regression analysis. The overall correctional equation has the following form (result of remaining 41 units),

$$\Delta SPM_{H2S} = 0.701 - 0.0824 \cdot \Delta t_{dp} - 0.374 \times SPM_{H2S} + 0.0185 \times \Delta t_{dp} \times SPM_{H2S} \ (R^2 = 0.9036) \qquad (14)$$

The H_2S concentrations predicted with the overall equation (eq. 14) and with the 41 different individual correctional equations of the 41 units were compared against the analyzer readings and are plotted in figure 7. Clearly the individual correctional equations gave appreciably better prediction results than the overall equation.

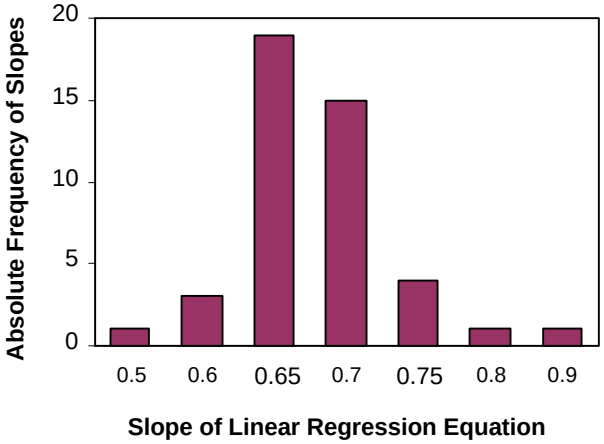

Figure 6. Distribution of linear regression equation slopes for 44 SPM units used to measure dry H_2S calibration gas (Mean = 0.651; Standard Deviation = 0.058).

Field Evaluation

Hydrogen Sulfide

Over 1500 observations were collected at t_{dp} of −10°C to 8°C, with the t_{dp} distribution shown in figure 8. Most (68%) of the measured H_2S readings were lower than 10 ppb (fig. 9). Two units malfunctioned after 5 or 7 days of operation. Thus, data analysis was based on the remaining eight units.

Overall, H_2S readings by the SPMs were about 70% of those as measured by the analyzer (table 4). The relatively lower concentration values registered by the SPMs (as−is) mainly resulted from the low t_{dp} of the sample air under this field measurement condition. This field result was consistent with the lab test results where the SPMs displayed approximately 66% and 80% of the analyzer readings when the sample air has a t_{dp} of −22°C and 9°C, respectively.

Readings from the eight SPMs were corrected using either the individual correctional equations or the overall correctional equation derived from the laboratory evaluation. Results showed that SPM readings less than 10 ppb were better off not to be corrected. Therefore, only readings between 10 and 90 ppb were corrected. The results were compared with the analyzer readings and linear equations were established (table 4). The individually corrected readings ranged from 0.89 to 1.13 (mean of 0.995, R^2= 0.95) of the analyzer readings, whereas the overall corrected readings ranged from 0.90 to 1.07 (mean of 0.973, R^2= 0.95) of the analyzer readings. Results in table 4 show that H_2S readings by SPMs can be corrected with the overall correctional equation derived from lab evaluation to achieve 90% to 107% agreement with the analyzer readings. A segment of as−is and corrected readings for unit serial number (SN) 3446 are shown in figure 10.

Ammonia

During the first field test at the poultry facility, 8 h of data were collected before the dew−point hygrometer malfunctioned. Ammonia levels were in the range of 3.4 to 5.4 ppm, and t_{dp} was in the range of 4°C to 7°C. Two SPMs malfunctioned due to tape failure. Data were analyzed for the remaining six units.

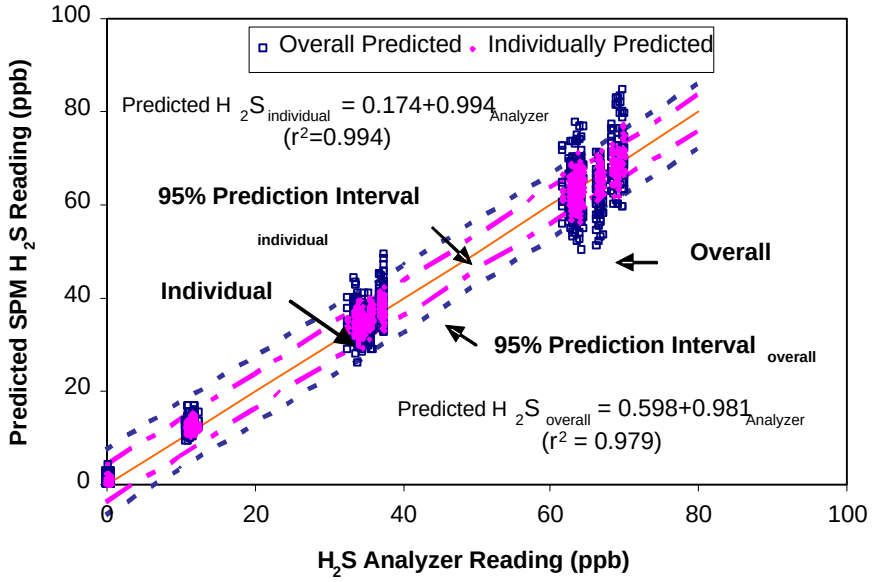

Figure 7. Corrected H_2S readings with overall regression equation vs. individual regression equations, and the respective 95% prediction intervals.

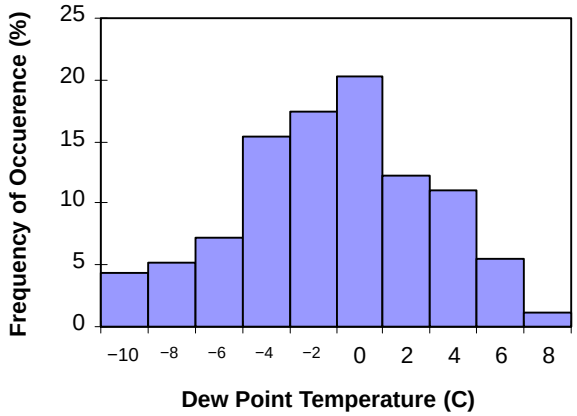

Figure 8. Distribution of dew−point temperatures of the sample air during field evaluation of Single Point Monitors (SPMs).

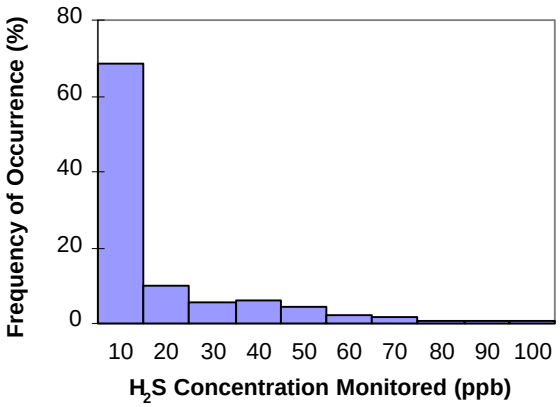

Figure 9. Distribution of H_2S concentrations in sample air under field evaluation of Single Point Monitors (SPMs).

Concentration was relatively constant during the 8−h operation at the poultry facility (fig. 11). Therefore, hourly averages of as−is readings were calculated and results are listed in table 5. All six SPMs showed slightly higher corrected readings during the first two hours of measurement (table 5). The reasons were unknown. In general, as−is readings of the SPMs were higher than the analyzer readings ($P < 0.05$). Corrected NH_3 concentrations from five units were not significantly different from the analyzer readings ($P > 0.05$).

Ammonia concentrations and t_{dp} for the field test at swine facility are shown in table 6. It can be noted that as−is readings of the SPMs tended to overestimate NH_3 concentration. However, application of the derived regression equations over−corrected the readings, thereby resulting in significantly lower corrected readings (slopes of 0.59 to 0.90).

Table 4. Slopes of linear equations relating Single Point Monitor (SPM) as−is and corrected readings to pulsed−fluorescence analyzer values during H_2S field test.

SPM	As−is		Individual Correction		General Correction	
Serial Number	Slope	R^2	Slope	R^2	Slope	R^2
3085	0.693	0.980	0.911	0.953	0.967	0.956
3132	0.709	0.980	0.971	0.940	0.978	0.951
3465	0.701	0.983	0.990	0.963	0.980	0.964
3497	0.761	0.980	0.891	0.956	1.074	0.952
3446	0.679	0.979	1.010	0.946	0.965	0.953
3318	0.647	0.976	1.074	0.937	0.899	0.949
3118	0.683	0.982	1.130	0.948	0.936	0.958
3496	0.704	0.980	0.979	0.950	0.982	0.946
Mean	0.697	0.980	0.995	0.949	0.973	0.954
Standard Deviation	0.032	0.002	0.079	0.008	0.050	0.006

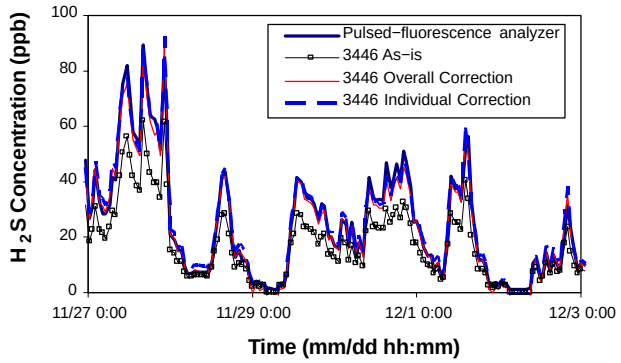

Figure 10. Profiles of H_2S concentration readings by a SPM (SN3446) in the form of as−is, individually corrected, or corrected by the overall equation and by the pulsed−fluorescence analyzer.

The SPM NH_3 readings for lower concentrations and low t_{dp} at the poultry facility were improved after correction with the regression equations. However, this was not the case for SPM NH_3 readings at higher concentration and higher t_{dp} conditions at the swine facility. It remains unknown whether the gas samples from the swine building caused interference with the NH_3 measurement, or the chemcassette tape had partially lost sensitivity due to aging.

Stability Evaluation

Under dry H_2S gas conditions, some SPMs exhibited positive changes while others exhibited negative changes (table 7). Absolute values were taken in determining relative changes and the averages of the changes for 25 SPMs at various levels were computed (fig. 12). Changes between 10 and 70 ppb were less than 12%. The larger change at zero level was mainly due to the small denominator. Slopes and intercepts from three units (12%) were significantly different at $P < 0.05$. However, all units were not significantly different at significance level of 0.01. In general, the SPMs exhibited good stability.

Conclusions

Operational performance of Single Point Monitors (SPMs) for measuring aerial NH_3 and H_2S levels was evaluated under laboratory and field conditions. Chemiluminescence NH_3 analyzer and pulsed−fluorescence H_2S analyzer were used as references of the comparisons. The following conclusions were drawn.

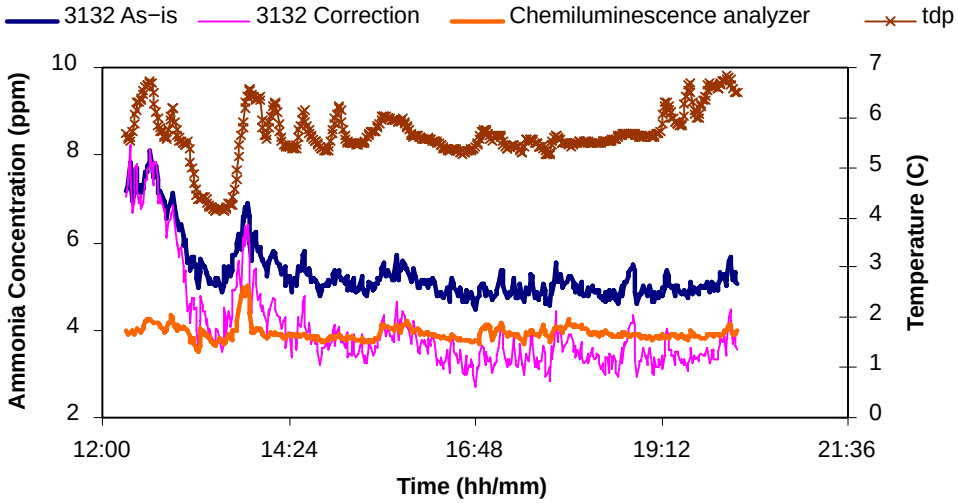

Figure 11. Profiles of NH_3 concentration readings by a SPM (SN 3132) in the form of as−is or individually corrected (for moisture) and by the chemiluminescenceanalyzer at a poultry facility.

Table 5. Hourly average ammonia concentrations from six Single Point Monitors (SPMs) and the chemiluminescence analyzer (TEI) during field test at a poultry production site.

		3134		3318		3118		3132		3317DC[a]		3496DC[a]	
Time	TEI	As−is	Crt[b]	As−is	Crt	As−is	Crt	As−is	Crt	As−is	Crt	As−is	Crt
12:18	4.0	6.4	5.6	7.1	7.3	6.0	7.6	6.8	6.4	8.2	6.7	7.4	7.0
13:18	4.0	5.4	4.0	5.9	5.5	6.0	5.8	5.6	4.6	6.9	5.2	6.2	5.4
14:18	3.8	5.0	3.4	5.3	4.4	5.5	4.9	5.2	3.8	6.1	3.9	5.6	4.4
15:18	3.9	5.0	3.3	5.3	4.3	5.5	4.8	5.2	3.8	5.9	3.8	5.5	4.2
16:18	3.9	4.6	2.9	5.0	3.8	5.2	4.5	4.9	3.3	5.5	3.2	5.2	3.9
17:18	4.0	4.7	3.0	5.0	4.0	5.2	4.5	5.0	3.5			5.3	4.0
18:18	3.9	4.6	2.8	4.9	3.7	5.1	4.3	4.9	3.4			5.1	3.7
19:18	3.9	4.8	3.0	5.1	3.9	5.2	4.3	5.0	3.5			5.8	4.5
Average	3.9	5.1[c]	3.5	5.4[c]	4.6	5.5[c]	5.1[c]	5.3[c]	4.0	6.5[c]	4.6	5.8[c]	4.6
S.D.[d]	0.07	0.60	0.92	0.73	1.23	0.35	1.12	0.63	1.02	1.05	1.41	0.73	1.09

[a] DC = duty cycle.
[b] Crt = corrected.
[c] Significant at $P < 0.05$.
[d] S.D. = standard deviation.

Table 6. Field condition for NH_3 measurement and slopes of linear relationships between SPM as−is readings and chemiluminescence analyzer.

Serial No.	Hours of Operation	Concentration Range (ppm)	t_{dp} Range (°C)	As−is		Individual Correction	
				Slope	R^2	Slope	R^2
3134	16	8−23	8−13	1.052	0.653	0.901	0.601
3318	15			0.953	0.595	0.904	0.559
3118	10	12−18	10−16	1.154	0.714	0.751	0.748
3132	17			1.282	0.886	0.829	0.898
3496DC[a]	66	8−23	8−17	[b]	[b]		
3446DC	23	7−18	10−16	1.013	0.451	0.586	0.85

[a] DC = duty cycle.
[b] No correlation could be established.

Table 7. Maximum and minimum relative changes of H_2S readings at nominal levels from 25 SPMs between 8−month period.

H_2S Analyzer Reading (ppb)	Relative Change (%)	
	Min	Max
0	−77.11	17.66
10	−21.07	7.79
20	−14.75	6.77
40	−10.79	6.18
60	−9.33	5.96
70	−8.89	6.56

- Regression equations were developed that relate SPM readings to those of the reference analyzers for calibration gas or sample air with different moisture contents.
- SPM readings of H_2S or NH_3 gas concentrations increase with moisture content of sample air. However, compensation for this moisture dependence can be made for H_2S gas measurement with an overall correctional equation to generally achieve 90% to 107% agreement with readings measured by the pulsed−fluorescence analyzer. In comparison, such correctional compensation was not effective for NH_3 measurement (59% to 90% agreement).
- Knowledge of moisture content in sample air is necessary to compensate for the moisture interference.
- SPMs showed weak interchangeability, especially for NH_3 measurement. However, the SPMs showed good stability over the 8−month testing period.

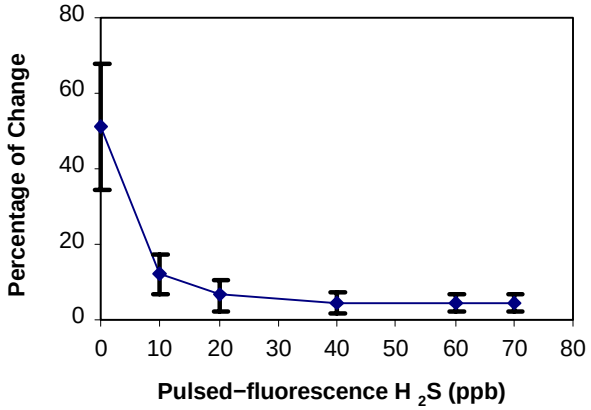

Figure 12. Relative changes (%) of H_2S readings from 25 SPM units at nominal levels of 0 to 70 ppb H_2S during an 8−month period. Vertical bars represent standard deviations (Calculation based on absolute values).

Acknowledgements

Funding for the study was provided by the National Pork Board and is acknowledged. The authors wish to thank Andrew Gray, undergraduate research assistant of ABE, for his assistance with data collection and analysis, and to Alyssa Rossnagel, undergraduate research intern, for her contribution to the data collection.

References

Amon, B., T. Amon, J. Boxberger, and C. Alt. 2001. Emission of NH_3, N_2O and CH_4 from dairy cows housed in a farmyard manure−tying stall (housing, manure storage, manure spreading). *Nutrient Cycling in Agroecosystems* 60(2): 103−113.

Bicudo, J. R., C. L. Tengman, D. R. Schmidt, and L. D. Jacobson, 2002. Ambient concentrations near swine barns and manure storage. ASAE Paper No. 024059. St. Joseph, Mich.: ASAE.

Chung, Y. C., C. Huang, and C. Tseng. 1996. Reduction of H_2S/NH_3 production from pig feces by controlling environmental conditions. *J. Environ. Sci. Health.* A31(1): 139−155.

Demmers, T. G. M., L. R. Burgess, J. L. Short, V. R. Philips, J. A. Clark, and C. M. Wathes. 1999. Ammonia emissions from two mechanically ventilated UK livestock buildings. *Atmospheric Environ.* 33(2): 217−227.

Hansen, M. N., M. Maahn, and M. H. Kaadt. 2003. Evaluation of the photoacoustic multi−gas monitor during measurements of gas emissions from composting livestock manure. *Proc. of International Symposium on Gaseous and Odor Emissions from Animal Production Facilities.* Bonn, Germany: CIGR.

Hinz, T., and S. Linke. 1998. A comprehensive experimental study of aerial pollutants in and emissions from livestock buildings. Part 1: Methods. *J. Agric. Eng. Res.*70(2): 111−118.

Jacobson, L. D., A. J. Heber, Y. Zhang, J. Sweenten, J. Kozie, S. J. Hoff, D. S. Bundy, D. B. Beasley, and G. R. Baughman. 2003. Air pollutant emissions from confined animal buildings in the U.S. *Proc. of International Symposium on Gaseous and Odor Emissions from Animal Production Facilities.* Bonn, Germany: CIGR.

Koelsch, R. K., B. L. Woodbury, D. E. Stenberg, D. N. Miller, and D. D. Schulte. 2004. Total reduced sulfur concentrations in the vicinity of beef cattle feedlots. *Applied Engineering in Agriculture* 20(1): 77−85.

Predicala, B. Z., R. G. Maghirang, S. B. Jerez, J. E. Urban, and R. D. Goodband. 2001. Dust and bioaerosol concentrations in two swine−finishing buildings in Kansas. *Transactions of the ASAE* 44(5): 1291−1298.

Rhoades, M. B., D. B. Parker, and B. Dye. 2003. Measurement of hydrogen sulfide in beef cattle feedlots on the Texas high plains. ASAE Paper No. 034108. St. Joseph, Mich.: ASAE.

Schmidt, D. R., L. D. Jacobson, and K. A. Janni. 2002. Continuous monitoring of ammonia, hydrogen sulfide and dust emissions from swine, dairy and poultry. ASAE Paper No. 024060. St. Joseph, Mich.: ASAE.

Stowell, R. R., H. Keener, P. R. Goodrich, and S. Foster. 2002. Gas and odor emissions from high−rise and deep−pit swine finishing facilities. ASAE Meeting Paper 024122. St. Joseph, Mich.: ASAE.

Wathes, C. M., M. R. Holden, R. W. Sneath, R. P. White, and V. R. Philips. 1997. Concentrations and emission rates of aerial ammonia, nitrous oxide, methane, carbon dioxide, dust and endotoxin in UK broiler and layer houses. *British Poultry Sci.*, 38(1): 14−28.

Zhu, J., L. Jacobson, D. Schmidt, and R. Nicolai. 2000. Daily variation in odor and gas emissions from animal facilities. *Applied Engineering in Agriculture* 16(2): 153−158.